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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/296,835	04/22/1999	RONALD A. WEIMER	M4065.0319/P319	8895
24998	7590	07/29/2004	EXAMINER	
DICKSTEIN SHAPIRO MORIN & OSHINSKY LLP			KIELIN, ERIK J	
2101 L STREET NW			ART UNIT	
WASHINGTON, DC 20037-1526			PAPER NUMBER	
			2813	

DATE MAILED: 07/29/2004

Please find below and/or attached an Office communication concerning this application or proceeding.

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Office Action Summary	Application No. 09/296,835	Applicant(s) WEIMER ET AL.	
	Examiner Erik Kielin	Art Unit 2813	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 03 June 2004.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 2-5,8,10-12 and 42-44 is/are pending in the application.
- 4a) Of the above claim(s) 43 is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 2-5,8,10-12,42 and 44 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- * See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|--|---|
| 1) <input type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____ |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | 5) <input type="checkbox"/> Notice of Informal Patent Application (PTO-152) |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)
Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____ |

DETAILED ACTION

This action responds to the Amendment filed 3 June 2004.

Election/Restrictions

1. Newly submitted claim 43 is directed to an invention that is independent or distinct from the invention originally claimed for the following reasons:

Each of the claims examined in the previous 8 Office actions are directed to depositing an oxygen deficient dielectric layer having a $k > 25$ and then wet oxidizing the dielectric layer using plural species of steam formation. Now, amended claim 43 recites,

“depositing **an oxygen-deficient dielectric film** having a dielectric constant of at least about 25 over an underlying layer; subjecting **a non-crystalline dielectric film** to a wet oxidation with steam...” (emphasis added)

which is now directed to deposition of **one** film and wet oxidizing treatment of **another** film.

Since applicant has received **numerous actions** on the merits for the originally presented invention, this invention has been constructively elected by original presentation for prosecution on the merits. Accordingly, claim 43 is withdrawn from consideration as being directed to a non-elected invention. See 37 CFR 1.142(b) and MPEP § 821.03.

Claim Rejections - 35 USC § 112

2. Claims 42 and 43 are rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the written description requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant

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art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

Regarding claim 42, the instant specification fails to provide support for using only “hydrogen and oxygen gases.” In this regard, the specification states at p. 8, lines 18-25,

“If a mixture of H₂ and O₂ gases is used to form the steam, suitable ratios of H₂ gas to O₂ gas are in the range of about 0.1 to about 0.80... The ratio of steam relative to **other gases** in the chamber 50 **should be at least as high as 0.005**, and **preferably is in the range of about 0.1 to about 0.5**, although lesser or greater amounts also can be used.”
(Emphasis added.)

Accordingly, there exists no support for using **only** hydrogen and oxygen since the specification indicates that “other gases” should be present, thereby teaching away from “**only** hydrogen and oxygen.”

Moreover, the claim specifically recites, “said steam provided in a ratio of at least 0.005 relative to **other gases present in the rapid thermal process chamber...**” (emphasis added).

Accordingly, the claim is internally contradictory. If the mixture is a “mixture of **only** hydrogen and oxygen gases,” then it cannot also include “steam” and “other gases.”

Claim Rejections - 35 USC § 103

3. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

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4. Claims 8, 2-5, 10-12, **42**, and **44** are rejected under 35 U.S.C. 103(a) as being unpatentable over **Patel** et al. (US 5,374,578) in view of either of **Emesh** et al. (US 5,728,603) and **Chivukula** et al. (US 6,066,581), and further in view of the excerpt from the basic textbook of **Van Zant**, (Microchip Fabrication, A Practical Guide to Semiconductor Processing, 3rd ed. McGraw-Hill: New York, 1997, pp. 157-160) and considered with the CRC Handbook of Chemistry and Physics 63rd Edition, CRC Press: Boca Raton FL, pp. D-196 to D-197 (used for a showing of inherency only).

Regarding independent claims **8**, **42**, and **44**, **Patel** discloses a method of forming a semiconductor device comprising,

forming an oxygen deficient dielectric (called “ferroelectric”) film **14** (Figs. 2-6) such as PZT which inherently has a dielectric constant of greater than 25 (see **Emesh** col. 8, Table 1 which teaches the dielectric constant of PZT, the same ferroelectric in **Patel**);

subjecting the dielectric film to an oxidation in “[g]ases like oxygen, ozone or air” (column 4, lines 10-11) using RTA (rapid thermal annealing), which must necessarily occur, then, in an RTA chamber at a temperature range of 650-850 °C for about 5-30 seconds (as further limited by instant claims 2-4) in order to increase the oxygen content of the ferroelectric film (column 2, lines 30-33), wherein **any pressure** may be used (col. 4, lines 24-27) during the annealing, which reads on pressures in the range from 0.001 Torr to less than 760 Torr (atmospheric pressure); and

performing a stabilizing treatment in a rapid thermal annealing chamber using oxygen anneal either before or after the ozone anneal (column 4, lines 23-29) --as further limited by instant claims 10 and 12.

Patel does not teach using wet oxidation to anneal the ferroelectric PZT layer **14**.

Emesh teaches forming an oxygen deficient ferroelectric material such as PZT; subjecting the dielectric film to a wet oxidation using a mixture comprising water and ozone in a rapid thermal annealing (RTA) chamber in order to reduce the temperature at which the ferroelectric material densifies/crystallizes and also to reduce the stress in the ferroelectric film and improves its the electrical properties (column 5, lines 50-67) which also inherently increases the oxygen content of the film as indicated by the reduced leakage current (sentence bridging columns 3-4).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate water during the ozone anneal of **Patel** for the reasons indicated in **Emesh** which includes at least reducing the stress in the ferroelectric film and improving the electrical properties such as increased dielectric constant (column 5, lines 50-67; col. 8, Table 1).

Similarly, **Chivukula** teaches forming an oxygen deficient ferroelectric material such as PZT; subjecting the dielectric film to a wet oxidation using a mixture comprising water and ozone at a temperature of 450-650 °C in a rapid thermal annealing (RTA) chamber for 30 seconds to several minutes to form uniform grain sizes in the ferroelectric material in a shorter time, at reduced temperature and superior characteristics during high frequency use compared to using dry oxidation (column 14, lines 27-48). (See also column 13, lines 30-53.)

It would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate water during the ozone anneal of **Patel** to provide a ferroelectric capacitor with superior characteristics during high frequency use as compared to using the dry oxidation used in **Patel**, as taught by **Chivukula**.

Furthermore, each of **Emesh** and **Chivukula** teaches that

“Water vapour was conveniently introduced into the annealing atmosphere of the rapid thermal anneal (RTA) system during the annealing of the PZT by passing oxygen (O₂) through a double bubbler containing purified deionized water, so that the oxygen was saturated with water vapour, e.g. using a gas flow rate of about 2 L/min.” (Emesh col. 5, lines 14-28; Chivukula, col. 13, lines 40-46).

It is held absent evidence to the contrary that the steam is present in an amount greater than about 0.005 (0.5%) relative to the other gases in the chamber. Support to show inherency can be easily determined from data in the Handbook of Chemistry and Physics. Pages D-196 and D-197 of the **CRC** (63rd edition) provide a Table having the vapor pressure of water as a function of temperature at temperatures below 100 °C. Because each of **Emesh** and **Chivukula** teaches that the oxygen is “saturated with water” all that need be known is the temperature of the bubbler. Even if it is assumed that bubbler is as low as standard room temperature (i.e. 25 °C), the **CRC** table of Vapor Pressure of Water Below 100 °C, indicates that the partial pressure of water is 23.756 Torr. Since atmospheric pressure is 760 Torr, the partial pressure of water in water-saturated oxygen is $23.756/760 \approx 0.0313$ or (3.13 %). Typically bubblers are heated indicating even high partial pressures of water. Accordingly, the water vapor is inherently greater than 0.005 relative to the other gases based upon the teachings in each of **Emesh** and **Chivukula**. (See MPEP 2112.)

Patel in view of either of **Emesh** and **Chivukula**, further, does not teach using a mixture of only hydrogen and oxygen gases that form steam, to form the steam. Instead, each of **Emesh** and **Chivukula** use a bubbler (**Emesh** at col. 5, lines 57-59; **Chivukula** at col. 13, lines 40-46).

Van Zant teaches that “Dryox,” a mixture of hydrogen and oxygen gases which react to form a steam oxidizing mixture in the reactor, is preferred over liquid systems such as a bubbler,

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because the process is cleaner and more controllable and also that “Dryox is the preferred method for production of advanced devices.” (See pp. 157-160 -- especially page 160.)

It would have been obvious to one of ordinary skill in the art at the time the invention was made to use hydrogen and oxygen as taught by **Van Zant** to form the steam for the wet oxidation mixture of either of **Emesh** and **Chivukula**, for the reasons indicated in **Van Zant**, as noted and especially because “Dryox” is preferred to bubblers which **Emesh** and **Chivukula** use.

Additionally, since each of **Emesh** and **Chivukula** teach a small additional amount of ozone, the limitation of “wet oxidation with only a mixture of hydrogen and oxygen gases that form steam” is met because ozone is an oxygen gases that reacts with hydrogen to form steam.

Furthermore, the method by which the water for the wet oxidizing atmosphere is not critical according to Applicant's admissions in the instant specification. Rather, Applicant's specification teaches away from such unexpected results. Applicant teaches,

“One of several techniques can be used to provide steam to a vicinity of the insulating film. Such techniques include using a **bubbled water vapor system**, a **pyrogenic system** or a **catalytic system**, or **generating steam in the chamber *in situ***.” (Emphasis added. See instant specification, page 3, lines 13-17.)

In other words, any of the presently notoriously well-known means to form the steam, which are specifically used in the art for oxidation, could be used, according to Applicant. Also note that the paragraph bridging pages 7 and 8 of Applicant's specification indicates specifically that a bubbler can be used in the instant invention.

Then further regarding claim 8, and additionally regarding claim 5, the ratio of hydrogen to oxygen is not taught in **Patel**.

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However, each of **Emesh** and **Chivukula** indicate that the wet oxidation is carried out in water plus oxygen and ozone (**Emesh** at col. 5, lines 19-28; **Chivukula** at col. 13, lines 36-46). “[I]n considering the disclosure of a reference, it is proper to take into account not only specific teachings of the reference but also the inferences which one skilled in the art would reasonably be expected to draw therefrom.” *In re Preda*, 401 F.2d 825, 826, 159 USPQ 342, 344 (CCPA 1968) See also *In re Lamberti*, 545 F.2d 747, 750, 192 USPQ 278, 280 (CCPA 1976). With this in mind, because each of **Emesh** and **Chivukula** teach that oxygen must be in excess of the water vapor, one of ordinary skill would know, based upon the stoichiometry of the reaction between hydrogen and oxygen to form the “Dryox” mixture containing water (as taught by **Van Zant**) that the ratio of hydrogen to oxygen must necessarily be less than or equal to about 0.67 because hydrogen reacts with oxygen in a 2 to 1 stoichiometric ratio ($2 \text{ H}_2 + \text{O}_2 \rightarrow 2 \text{ H}_2\text{O}$). Otherwise, the oxygen will be depleted in the formation of water and excess hydrogen would remain, contrary to the teaching in each of **Emesh** and **Chivukula**. Accordingly, one of ordinary skill would clearly recognize that using the more desirable method of “Dryox” oxidation, as taught by **Van Zant**, would necessarily require a range hydrogen to oxygen of 0.67 or less in order to achieve the mixture taught by each of **Emesh** and **Chivukula** which requires excess oxygen with the water, which overlaps the claimed ratio of 0.1 to 0.8 (instant claim 8) and 0.1 to 0.5 (instant claim 5).

Further regarding claims 2-4, although **Patel** does not recite Applicant’s exact ranges of either 450-750 °C or 750-900 °C or exact times of 20-60 seconds for the oxidation, **Patel** does disclose an overlapping temperature range of 650-850 °C and time range of 5-30 seconds, in at least one example. **Emesh** teaches 300 seconds, which is a function of the lower temperatures

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used. **Chivukula** teaches 30 seconds to several minutes, which are, again, temperature and material dependent. These claims are *prima facie* obvious without showing that the claimed ranges achieve unexpected results relative to the prior art range. *In re Woodruff*, 16 USPQ2d 1935, 1937 (Fed. Cir. 1990). See also *In re Aller*, 105 USPQ 233 (CCPA 1955) (selection of optimum ranges within prior art general conditions is obvious).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to optimize the temperature and anneal time to provide the best ferroelectric film, according to the precedent above and the teachings in **Emesh** and **Chivukula** that the temperatures and times are material dependent. Also note, although **Emesh** teaches an ozone/water oxidizing temperature of 500 °C or less, **Emesh** also teaches that increasing the temperature at which the wet oxidation occurs increases the dielectric constant of the high dielectric constant film (column 8, lines 6-12) which is desired in the semiconductor device fabrication art especially for fabricating capacitors for DRAM devices. Accordingly, one of ordinary skill would be motivated to use higher temperatures than 500 °C, as suggested by **Emesh** to increase the dielectric constant of the ferroelectric layer to enable smaller capacitors to be formed, which in turn enables further miniaturization of semiconductor devices using capacitors.

Regarding claim 11, **Patel** does not teach performing the ozone oxidizing or the oxygen stabilizing treatments at different temperatures, but each of **Emesh** and **Chivukula** teaches that the addition of water vapor reduces the densification/crystallization temperature from dry conditions.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to perform the wet ozone anneal of **Patel** in view of **Emesh** and **Chivukula** at a lower temperature than the oxygen stabilizing anneal, because each of **Emesh** and **Chivukula** teaches a lower temperature may be used for wet versus dry oxidation, and provides examples of temperatures lower than in **Patel**.

Response to Arguments

5. Applicant's arguments filed 3 June 2004 have been fully considered but they are not persuasive.

Applicant argues that the applied references do not teach the wet oxidation limitation of "only a mixture of hydrogen and oxygen gases that form steam." Examiner respectfully disagrees. Factually, oxygen and ozone and hydrogen form steam, ozone being even more reactive than oxygen because ozone itself is highly unstable. Even if it were to be assumed that ozone did not react with hydrogen to form steam, ozone still would not prevent the oxygen from forming steam. Accordingly, the limitation, as presently recited is literally met by the applied references. Moreover, this limitation is recited only in claims 8 and therefore in dependent claims 2-5 and 10-12. Accordingly, these arguments do not reflect the limitations in claims 42 and 44.

Applicant argues that **Patel** teaches away from each of **Emesh** and **Chivukula** based upon the annealing temperature and the requirement for dissociation of ozone. Examiner respectfully submits that Applicant fails to recognize that each of **Emesh** and **Chivukula** uses ozone, which serves its purpose. One of ordinary skill would recognize that the ozone will react at lower

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temperatures due to the presence of water, as taught in each of Emesh and Chivukula.

Accordingly the argument is not persuasive.

Examiner respectfully disagrees that Emesh fails to teach using temperatures greater than 500 °C for reasons already indicated. (See, for example, Emesh, col. 5, last paragraph.)

Accordingly the argument is not persuasive.

Examiner notes with interest that the instant application will have the same problems that Applicant accuses Emesh of having by oxidation at a higher temperature (REMARKS, p. 9, last paragraph) and further notes that the instant specification wholly fails to address the criticality of the temperature ranges. Verily the instant specification teaches that temperatures of 450 °C to 950 °C will work. Accordingly, it is incumbent upon Applicant to come forth with evidence of some unexpected result for the temperature range. Given the problem presently recognized by Applicant in Emesh, it would appear that Emesh only provides support that the result is undesirable.

Applicant argues that Chivukula uses sol-gel precursors. So does Patel (Patel, col. 3, lines 59-63). This is not a teaching away.

Applicant's argument that the temperature in Chivukula and Emesh is too low for the hydrogen and oxygen to react to form steam is only an admission by Applicant that the instant claims are not enabled. It is unclear how Applicant can argue that a temperature of 450 °C will work to react hydrogen and oxygen in the instant invention but will somehow not react in the invention of another. This is factually in error.

The arguments regarding claims 42-44 are noted and are incomplete. Merely reciting the claims is not an argument as to how the instant claims are patentably distinguished over the applied art.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Erik Kielin whose telephone number is 571-272-1693. The examiner can normally be reached on 9:00 - 19:30.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Carl Whitehead, Jr. can be reached on 571-272-1702. The fax phone number for the organization where this application or proceeding is assigned is 703-872-9306.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).



Erik Kielin
Primary Examiner
26 July 2004